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Kinetic theory derivation of transport equations for gases with internal energy

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Multitemperature models are widely used in the aerospace community to model atmospheric entry flows. In this paper, we propose a general description of the internal energy excitation of a molecular gas in thermal nonequilibrium by distinguishing between slow and fast collisions. A multiscale Chapman-Enskog method is used to study thermalization and derive Euler equations of conservation of mass, momentum, translational energy and internal energy. As opposed to conventional perturbation methods, the fast collision operator is expanded in the small parameter used to define the threshold for the net energy for fast collisions. We show that the role of the fast collisions is to thermalize the translational and internal energy modes, whereas the role of the slow collisions is to contribute to the thermal relaxation of the translational and internal energy modes.

I. Introduction

KINETIC theory is a powerful tool to derive macroscopic conservation equations for complex multiphysics systems, such as atmospheric entry plasmas. It also allows to link the transport fluxes to the interaction potentials that govern the collisions taking place among the gas particles. For instance, the transport fluxes (diffusion of mass, momentum, and energy) found in the Navier-Stokes equations are related to macroscopic forces (electric field, gradients of pressure, temperature, velocity, and species concentrations) by proportionality coefficients called transport properties (diffusion coefficients, thermal diffusion ratios, viscosity, and thermal conductivity). Relevant collision integrals constitute the set of data for the transport properties. Closure of the macroscopic conservation equations is realized by computing the collision integrals at the microscopic level, based on either the interaction potentials or the cross-sections obtained from experimental measurements and ab initio calculations. In the case of chemically reacting flows with internal degrees of freedom, the expressions for the chemical production terms and energy exchange terms can also be derived from a microscopic approach.

Multitemperature models are widely used in the aerospace community to model atmospheric entry flows.[2,7] These models have been developed based on experimental data obtained in flight and also in high-enthalpy facilities representative of specific flight conditions, such as in arc-jet and shock-tube windtunnels.[17] These flows are in strong nonequilibrium and the models developed contain ad-hoc terms valid only

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for some dedicated applications. In this paper, we propose a general description of the internal energy excitation of a molecular gas in thermal nonequilibrium based on kinetic theory. This work is part of a broader effort that aims at developing new models based on microscopic theory and applying them to macroscopic scale in computational fluid dynamics codes.[11,12,14,19] The basic principles of kinetic theory based on the Boltzmann equation have been generalized by Waldman, Wang Chang and Uhlenbeek[5,6,15] to gases with internal degrees of freedom. Deviation from thermo-chemical nonequilibrium in molecular flows has been studied later, for instance by Nagnibeda and Kustova[16] and Brun.[1] In strong nonequilibrium flows, the characteristic times for gas dynamics and relaxation processes become comparable, and therefore, the equations for macroscopic parameters of the flow should be coupled to the equations for physico-chemical kinetics.[16] A difficulty is to derive a proper scaling for the Boltzmann equation, that accounts for the different relaxation times. An elegant approach based on a dimensional analysis has been proposed by Petit and Darrozes[18] for the translational relaxation processes between the electrons and heavy particles in a plasma. The resulting scaling affects no only the differents terms of the streaming and collision operators of the kinetic equations, but also the collision operators themselves and the collisional invariants.[8] Degond and Lucquin[4] have expanded the collision operators in terms of the perturbation parameter driving nonequilibrium phenomena, such as the square root of the electron heavy-particle mass ratio for plasmas in translational nonequilibrium. When the Knudsen number is small enough, a multiscale Chapman-Enskog expansion method allows to derive conservation equations for continuum flows. Otherwise, rarefied gas effects can be described by means of Boltzmann moment systems with a closure assumption such as the Grad method, as shown in a companion paper.[13] A similar multiscale approach with expansion of the collision operators in the perturbation parameter has also been applied to study ionization phenomena.[9]

In this paper, a multiscale Chapman-Enskog method is proposed for the treatment of internal energy relaxation in a molecular gas. The co-existence of fast and slow collisions in the system results in thermal nonequilibrium between the translational and internal energy modes. In section II, the Boltzmann equation is presented for a gas of identical particles with internal degrees of freedom based on a quasi-classical approach. The scaling is derived based on a dimensional analysis. The collisions are divided in two categories based on the magnitude of the net internal energy. For fast collisions, this quantity is assumed to be lower than an energy threshold equal to a fraction of a characteristic thermal energy for the gas that is controlled by a small parameter. In section III, the study of the dynamics of a fast binary collision, yields the dependence of the particle velocities on the perturbation parameter. A lemma allows to split the internal energy of all the levels into perturbed elastic and inelastic contributions for the fast collisions. We proceed with a Chapman-Enskog expansion to describe the system based on a continuum approach. The Euler equations are derived with separate energy equations for the internal energy and kinetic energy. The proofs for the propositions and lemmas presented are not derived here, the paper objective is to introduce the physical concepts without the mathematical technicalities. Finally, conclusions review the contributions of the different types of collisions to the thermalization and thermal relaxation processes.

II. Boltzmann equation

A. Assumptions

The gas is composed of identical particles with internal degrees of freedom. Based on a quasi-classical approach, one assumes that the particles may have only certain discrete internal energy levels. These levels are labelled with an index i and the set of indices is denoted by I. Quantity $E_i^\star$ stands for the energy of level i, and a_i, its degeneracy. Dimensional quantities are denoted by the superscript *. The proposed model relies on the following set of assumptions:

1. There are no external forces.

2. The reactive collisions are not accounted for.

3. The inert particle interactions are binary encounters modeled by means of a Boltzmann collision operator: $(i,j) \rightleftharpoons (i',j')$, $i,j,i',j' \in \mathrm{I}$, where (i,j) and (i',j') are ordered pairs of energy levels for the interacting particles. The net internal energy through the collision is defined by the expression $E_{ij}^{i'j'\star} = E_{i'}^\star + E_{j'}^\star - E_i^\star - E_j^\star$.

4. The collisions are divided in two categories based on the magnitude of the net internal energy. For fast collisions, this quantity is assumed to be lower than an energy threshold equal to a fraction of a characteristic thermal energy for the gas: $|E_{ij}^{i'j'\star}| \leq \varepsilon \mathrm{k_B} T^0$, where symbol ε is a small parameter. Quantity T^0 stands for a reference temperature, and $\mathrm{k_B}$, Boltzmann's constant. For slow collisions, the net internal energy is assumed to satisfy the relation $|E_{ij}^{i'j'\star}| > \varepsilon \mathrm{k_B} T^0$.

5. The fast collisions are characterized by a reference differential cross-section σ^0. The slow collisions are assumed to have a reference differential cross-section equal to a fraction of the one of the fast collisions: $\varepsilon\sigma^0$; this assumption is made to account for the threshold energy that is used to define the lower bound for the relative kinetic energy.[10]

6. The macroscopic time scale t^0 is assumed to be comparable with the kinetic time scale for fast collisions τ^0 divided by ε. The macroscopic length scale L^0 is based on a reference convective length $L^0 = v^0 t^0$, where quantity v^0 is a reference hydrodynamic velocity.

7. The pseudo Mach number, defined as the reference hydrodynamic velocity divided by the thermal speed, $M = v^0/V^0$, is supposed to be at least of order one.

The Knudsen number is defined as $K_n = l^0/L^0$, where symbol l^0 stands for the mean free path. The Knudsen number is proportional to ε, provided that assumption (6) is satisfied. Therefore, a continuum description of the system is deemed to be possible. Finally, the co-existence of fast and slow collisions in the system results in thermal nonequilibrium.

B. Streaming and collision operators

Following Ferziger and Kaper,[5] the collisions between the gas particles are divided in two categories: elastic and inelastic collisions. Through elastic collisions, the internal energy levels of both particles is conserved

$$(i,j) \rightleftharpoons (i,j), \quad i,j \in \mathrm{I}.$$

Through inelastic collisions, the internal energy state of one or both particles is changed

$$(i,j) \rightleftharpoons (i',j'), \quad i,j,i',j' \in \mathrm{I}, \quad (i',j') \neq (i,j).$$

The value of the net internal energy can span different orders of magnitude. In particular, inelastic collisions include resonant collisions through which the sum of the internal energy of the particle pair is conserved

$$E_{ij}^{i'j'\star} = 0.$$

Notice that the kinetic energy of the particle pair is also conserved in this case. The exchange collisions

$$(i,j) \rightleftharpoons (j,i), \quad i,j \in \mathrm{I},\ i \neq j,$$

are examples of possible resonant inelastic collisions. In general, the exchange of internal levels is not required for resonant inelastic collisions. Given assumption 4, fast collisions are defined based on their net internal energy that satisfies the relation $|E_{ij}^{i'j'\star}| \leq \varepsilon \mathrm{k_B} T^0$. They comprise elastic collisions and resonant inelastic collisions for which $|E_{ij}^{i'j'\star}| = 0$, as well as quasi-resonant inelastic collisions defined as the fast collisions with a non-zero net internal energy.

The velocity distribution function of a particle with an internal energy level i and velocity $\boldsymbol{c}_i^\star$ at time $t^\star$ and position $\boldsymbol{x}^\star$ is denoted by $f_i^\star = f_i^\star(t^\star, \boldsymbol{x}^\star, \boldsymbol{c}_i^\star)$. The temporal evolution of the velocity distribution function $f_i^\star$ is governed in the phase space by the Boltzmann equation

$$\mathcal{D}_i^\star(f_i^\star) = \mathcal{J}_i^\star(f^\star). \tag{1}$$

The streaming operator is the material derivative in the phase space

$$\mathcal{D}_i^\star(f_i^\star) = \partial_{t^\star} f_i^\star + \boldsymbol{c}_i^\star \cdot \boldsymbol{\partial}_{\boldsymbol{x}^\star} f_i^\star, \quad i \in \mathrm{I},$$

expressed here in an inertial reference frame. The collision operator is introduced as

$$\mathcal{J}_i^\star(f^\star) = \sum_{(j,i',j')\in \mathrm{I}^3} \mathcal{J}_{ij}^{i'j'\star}(f_i^\star, f_j^\star), \quad i \in \mathrm{I}, \tag{2}$$

where the set $\mathrm{I}^3 = \mathrm{I}\times\mathrm{I}\times\mathrm{I}$. The partial collision operator is given by the relation

$$\mathcal{J}_{ij}^{i'j'\star}(f_i^\star, f_j^\star) = \int \left(f_{i'}^\star f_{j'}^\star \frac{a_i a_j}{a_{i'} a_{j'}} - f_i^\star f_j^\star \right) W_{ij}^{i'j'\star} \mathrm{d}\boldsymbol{c}_j^\star \mathrm{d}\boldsymbol{c}_{i'}^\star \mathrm{d}\boldsymbol{c}_{j'}^\star.$$

Quantity $W_{ij}^{i'j'\star}$ is the transition probability for the direct collision $(i,j) \to (i',j')$. Sorting the collisions based on the magnitude of the total internal energy of the pair of particles, the Boltzmann eq. (22) can be rewritten as

$$\mathcal{D}_i^\star(f_i^\star) = \mathcal{J}_i^{\mathcal{F}\star}(f^\star) + \mathcal{J}_i^{\mathcal{S}\star}(f^\star), \quad i \in \mathrm{I}. \tag{3}$$

The fast collision operator $\mathcal{J}_i^{\mathcal{F}\star}$ for elastic collisions and resonant inelastic collisions is introduced as

$$\mathcal{J}_i^{\mathcal{F}\star}(f^\star) = \sum_{(j,i',j')\in\mathcal{F}_i} \mathcal{J}_{ij}^{i'j'\star}(f_i^\star, f_j^\star), \quad i \in \mathrm{I}.$$

The fast collisions associated with the energy level $i \in \mathrm{I}$ are denoted by the set of triplets for which the net internal energy is small, *i.e.*, elastic collisions, as well as resonant and quasi-resonant inelastic collisions,

$$\mathcal{F}_i = \{(j,i',j') \in \mathrm{I}^3 \text{ and } |E_{ij}^{i'j'\star}| \le \varepsilon \mathrm{k_B} T^0\},$$

The slow collision operator $\mathcal{J}_i^{\mathcal{S}\star}$ for non-resonant inelastic collisions, is defined as

$$\mathcal{J}_i^{\mathcal{S}\star}(f^\star) = \sum_{(j,i',j')\in\mathcal{S}_i} \mathcal{J}_{ij}^{i'j'\star}(f_i^\star, f_j^\star), \quad i \in \mathrm{I},$$

where the slow collisions are associated with the complement set of $\mathcal{F}_i$ relative to the set I^3

$$\mathcal{S}_i = \{(j,i',j') \in \mathrm{I}^3 \text{ and } |E_{ij}^{i'j'\star}| > \varepsilon \mathrm{k_B} T^0\}.$$

C. Collisional invariants

Although the number of particles in each energy level is not conserved in a collision, the total number of particles (mass), momentum, and total energy are. Defining the scalar collisional invariants

$$\begin{cases} \psi_i^{1\star} &= m^\star, \\ \psi_i^{1+\nu\star} &= m^\star c_{i\nu}^\star, \qquad\qquad \nu \in \{1,2,3\}, \\ \psi_i^{5\star} &= \frac{1}{2} m^\star \boldsymbol{c}_i^\star \cdot \boldsymbol{c}_i^\star + E_i^\star, \end{cases} \tag{4}$$

the following equality is satisfied $\psi_i^{l\star} + \psi_j^{l\star} = \psi_{i'}^{l\star} + \psi_{j'}^{l\star}$, $l \in \{1,\dots,5\}$. We introduce the scalar product

$$\langle\!\langle \xi^\star, \zeta^\star \rangle\!\rangle^\star = \sum_{j\in\mathrm{I}} \int \xi_j^\star \odot \bar{\zeta}_j^{\star} \, \mathrm{d}\boldsymbol{c}_j^\star, \tag{5}$$

for families $\xi^\star = (\xi_i^\star)_{i\in\mathrm{I}}$ and $\zeta^\star = (\zeta_i^\star)_{i\in\mathrm{I}}$. The symbol $\odot$ stands for the fully contracted product in space, and the symbol $\bar{}$ for the conjugate transpose operation. The collision operator $\mathcal{J}^\star = (\mathcal{J}_i^\star)_{i\in\mathrm{I}}$ defined in eq. (2) obeys the following property.

Property II.1 *The collision operator $\mathcal{J}^\star$ is orthogonal to the space of collisional invariants, i.e.,*

$$\langle\!\langle \psi^{l\star}, \mathcal{J}^\star \rangle\!\rangle^\star = 0, \text{ for all } l \in \{1,\dots,5\}.$$

Number density	n^0	Thermal speed	V^0
Fast-collision differential cross-section	σ^0	Fast-collision kinetic time scale	τ^0
Mean free path	l^0	Macroscopic time scale	t^0
Temperature	T^0	Macroscopic length	L^0
Mass	m^0	Hydrodynamic velocity	v^0

Table 1. Reference dimensional quantities.

The individual contributions to the total energy, *i.e.*, the kinetic energy $\frac{1}{2}m^\star \boldsymbol{c}_i^\star \cdot \boldsymbol{c}_i^\star$ and the internal energy $E_i^\star$, are not conserved through collisions.

The collisional invariants allow to introduce the flow macroscopic quantities mass, momentum, and total energy, as average microscopic quantities:

$$\begin{cases} \rho^\star & = \langle\!\langle f^\star, \psi^{1\star} \rangle\!\rangle^\star, \\ \rho^\star v_\nu^\star & = \langle\!\langle f^\star, \psi^{1+\nu\star} \rangle\!\rangle^\star, \qquad \nu \in \{1,2,3\}, \\ \frac{1}{2}\rho^\star |\boldsymbol{v}^\star|^2 + \rho^\star e^\star + \rho^\star \mathcal{E}^\star & = \langle\!\langle f^\star, \psi^{5\star} \rangle\!\rangle^\star, \end{cases} \tag{6}$$

where the thermal energy is the sum of the translational and internal energy

$$\begin{cases} \rho^\star e^\star & = \langle\!\langle f^\star, \frac{1}{2}m^\star |\boldsymbol{c}^\star - \boldsymbol{v}^\star|^2 \rangle\!\rangle^\star, \\ \rho^\star \mathcal{E}^\star & = \langle\!\langle f^\star, E^\star \rangle\!\rangle^\star. \end{cases} \tag{7}$$

D. Dimensional analysis

A sound scaling of the Boltzmann equation can be deduced from a dimensional analysis. Reference quantities, given in Table 2, are assumed to be common to all the species. At the microscopic scale, a characteristic number density n^0 and differential cross-section σ^0 for fast-collision are introduced. The mean free path is given by the expression $l^0 = 1/(n^0\sigma^0)$. The thermal speed is obtained by the following expression

$$V^0 = \sqrt{\frac{\mathrm{k_B} T^0}{m^0}},$$

where symbol m^0 stands for a characteristic mass. The mean free time is then computed as

$$\tau^0 = \frac{l^0}{V^0}.$$

Assumption (6) states that the macroscopic time scale reads

$$t^0 = \frac{\tau^0}{\varepsilon}.$$

A macroscopic length scale L^0 is also introduced based on a characteristic hydrodynamic velocity:

$$L^0 = v^0 t^0.$$

The ratio of the two characteristic times is thus

$$\frac{\tau^0}{t^0} = \varepsilon = MKn,$$

where the pseudo Mach number is $M = u^0/V^0$, and the Knudsen number, $Kn = l^0/L^0$. The pseudo Mach number is based on the characteristic flow velocity and the thermal speed, that is an estimate for the speed of sound. The perturbation parameter is assumed to be small enough, such that a continuum description of the system is possible, $\varepsilon \ll 1$, the gas is collision dominated.

Nondimensional variables are based on the reference quantities. They are denoted by dropping the superscript *. In particular, one has the following expression for the distribution function, $f_i^\star = n^0 f_i/(V^0)^3$, and particle velocity, $\boldsymbol{c}_i^\star = V^0 \boldsymbol{c}_i$, $i \in \mathrm{I}$. We investigate the system at the macroscopic time scale, $t^\star = t^0 t$, and macroscopic length scale, $\boldsymbol{x}^\star = L^0 \boldsymbol{x}$. The streaming operator of the Boltzmann eq. (22) can be expressed as

$$\mathcal{D}_i^\star(f_i^\star) = \frac{n^0}{(V^0)^3 t^0}\mathcal{D}_i(f_i), \quad i \in \mathrm{I},$$

where $\mathcal{D}_i(f_i) = \partial_t f_i + \boldsymbol{c}_i \cdot \partial_{\boldsymbol{x}} f_i$. The fast and slow collision operators are given by the expressions

$$\mathcal{J}_i^{\mathcal{F}\star}(f^\star) = \frac{(n^0)^2\sigma^0}{(V^0)^2}\mathcal{J}_i^{\mathcal{F}}(f), \qquad \mathcal{J}_i^{\mathcal{S}\star}(f^\star) = \frac{(n^0)^2\varepsilon\sigma^0}{(V^0)^2}\mathcal{J}_i^{\mathcal{S}}(f), \quad i \in \mathrm{I},$$

with the nondimensional operators

$$\mathcal{J}_i^{\mathcal{F}}(f) = \sum_{(j,i',j')\in\mathcal{F}_i} \mathcal{J}_{ij}^{i'j'}(f_i, f_j), \qquad \mathcal{J}_i^{\mathcal{S}}(f) = \sum_{(j,i',j')\in\mathcal{S}_i} \mathcal{J}_{ij}^{i'j'}(f_i, f_j), \quad i \in \mathrm{I}.$$

The nondimensional partial collision operator is introduced as

$$\mathcal{J}_{ij}^{i'j'}(f_i, f_j) = \int \left(f_{i'} f_{j'} \frac{a_i a_j}{a_{i'} a_{j'}} - f_i f_j \right) W_{ij}^{i'j'} \mathrm{d}\boldsymbol{c}_j \mathrm{d}\boldsymbol{c}_{i'} \mathrm{d}\boldsymbol{c}_{j'}.$$

The reference transition probability is $\sigma^0/(V^0)^5$ for fast collisions and $\varepsilon\sigma^0/(V^0)^5$ for slow collisions. Finally, the nondimensional Boltzmann equation is found to be

$$\mathcal{D}_i(f_i) = \frac{1}{\varepsilon}\mathcal{J}_i^{\mathcal{F}}(f) + \mathcal{J}_i^{\mathcal{S}}(f), \quad i \in \mathrm{I}. \tag{8}$$

The multiscale analysis occurs at three levels: a) In the righ-hand-side of the kinetic eq. 8; b) In the energy collisional invariant ψ_i^5 of eq. (8) for fast collisions; c) In the fast collision operator $\mathcal{J}_i^{\mathcal{F}}(f)$. Slow collisions are dealt with as usual. Fast collisions require a specific treatment presented in the following section. The net internal energy for collisions is given by the relation $|E_{ij}^{i'j'\star}| = \mathrm{k_B} T^0 |E_{ij}^{i'j'}|$.

III. Chapman-Enskog method

A. Preliminary results

The study of the dynamics of a fast binary collision, $(i,j) \rightleftharpoons (i',j') : i,j,i',j' \in \mathrm{I}$ and $|E_{ij}^{i'j'}| \leq \varepsilon$, yields the dependence of the particle velocities on the ε parameter. For fast collisions, the net internal energy is rescaled as $E_{ij}^{i'j'} = \varepsilon E_{ij}^{i'j'(1)}$ and the momentum and energy conservation is expressed by means of the relations

$$m\boldsymbol{c}_i + m\boldsymbol{c}_j = m\boldsymbol{c}_{i'} + m\boldsymbol{c}_{j'} \tag{9}$$

$$\tfrac{1}{2}m\boldsymbol{c}_i\cdot\boldsymbol{c}_i + \tfrac{1}{2}m\boldsymbol{c}_j\cdot\boldsymbol{c}_j = \tfrac{1}{2}m\boldsymbol{c}_{i'}\cdot\boldsymbol{c}_{i'} + \tfrac{1}{2}m\boldsymbol{c}_{j'}\cdot\boldsymbol{c}_{j'} + \varepsilon E_{ij}^{i'j'(1)}. \tag{10}$$

The velocities after collision are related to their counterpart before collision

$$\boldsymbol{c}_{i'} = \tfrac{1}{2}(\boldsymbol{c}_i + \boldsymbol{c}_j) + \tfrac{1}{2}(|\boldsymbol{c}_i - \boldsymbol{c}_j|^2 - 4\varepsilon E_{ij}^{i'j'(1)})^{1/2}\boldsymbol{\omega}, \tag{11}$$

$$\boldsymbol{c}_{j'} = \tfrac{1}{2}(\boldsymbol{c}_i + \boldsymbol{c}_j) - \tfrac{1}{2}(|\boldsymbol{c}_i - \boldsymbol{c}_j|^2 - 4\varepsilon E_{ij}^{i'j'(1)})^{1/2}\boldsymbol{\omega}, \tag{12}$$

where the direction of the relative velocities after collision in their center of mass is defined by

$$\boldsymbol{\omega} = \frac{\boldsymbol{c}_{i'} - \boldsymbol{c}_{j'}}{|\boldsymbol{c}_{i'} - \boldsymbol{c}_{j'}|}.$$

Equations (13) and (12) allow to derive the following relation for the relative kinetic energy

$$\tfrac{1}{2}|\boldsymbol{c}_i - \boldsymbol{c}_j|^2 = \tfrac{1}{2}|\boldsymbol{c}_{i'} - \boldsymbol{c}_{j'}|^2 + 2\varepsilon E_{ij}^{i'j'(1)}. \tag{13}$$

The relative kinetic energy $|\boldsymbol{c}_i - \boldsymbol{c}_j|^2/2$ is bounded from below by the energy $2\varepsilon E_{ij}^{i'j'(1)}$. This property allows to justify the reference differential cross-section for the fast collisions given in assumption 5.

The following lemma allows to split the internal energy of all the levels into perturbed elastic and inelastic contributions for the fast collisions.

Lemma III.1 (Perturbed energy for fast collisions) *For all energy level $i \in \mathrm{I}$, let us consider the fast collisions $(i,j) \rightleftharpoons (i',j')$, with $(j,i',j') \in \mathcal{F}_i = \{(j,i',j') \in \mathrm{I}^3 \text{ and } |E_{ij}^{i'j'}| \leq \varepsilon\}$. There is a perturbed energy $\hat{E}_i \in \mathbb{R}$ such that $|E_i - \hat{E}_i| \leq C\varepsilon$, where C is a constant, and such that for all the fast reactions, the net perturbed energy vanishes, i.e., $\hat{E}_{ij}^{i'j'} = 0$.*

The introduction of perturbed energy levels is crucial to separate the energy collision invariant into fast collisional invariants and to expand the fast collision operator in the small parameter ε used to define the threshold for the net energy for fast collisions. In turn, it allows for a generalization of the Chapman-Enskog method to gases with internal degrees of freedom in thermal nonequilibrium. It is important to mention that, in general, the energy $\hat{E}_i$ does not correspond to any existing quantum energy level. The fast scalar collisional invariants are introduced as

$$\begin{cases} \hat{\psi}_i^1 &= m, \\ \hat{\psi}_i^{1+\nu} &= m c_{i\nu}, \qquad \nu \in \{1,2,3\}, \\ \hat{\psi}_i^5 &= \frac{1}{2} m \boldsymbol{c}_i \cdot \boldsymbol{c}_i, \\ \hat{\psi}_i^6 &= \hat{E}_i. \end{cases} \tag{14}$$

Notice that the sum of the flow kinetic energy and translational energy is obtained based on the microscopic kinetic energy: $\frac{1}{2}\rho|\boldsymbol{v}|^2 + \rho e = \langle\!\langle f, \hat{\psi}^5 \rangle\!\rangle$. A perturbation of the macroscopic internal energy is obtained based on the microscopic perturbed energy: $\rho\hat{\mathcal{E}} = \langle\!\langle f, \hat{\psi}^6 \rangle\!\rangle$, with $\mathcal{E} = \hat{\mathcal{E}} + \mathcal{O}(\varepsilon)$

The collision operator $\mathcal{J}_i^{\mathcal{F}} = (\mathcal{J}_i^{\mathcal{F}})_{i\in\mathrm{I}}$ obeys the following property.

Property III.1 *The collision operator $\mathcal{J}^{\mathcal{F}}$ is orthogonal to the space of fast collisional invariants, i.e.,*

$$\langle\!\langle \hat{\psi}^l, \mathcal{J}^{\mathcal{F}} \rangle\!\rangle = 0, \text{ for all } l \in \{1,\ldots,6\}.$$

The individual contributions to the total energy, *i.e.*, the kinetic energy and the perturbed internal energy, are thus separately conserved through fast collisions.

The fast collision operator can be expanded into the ε parameter.

Theorem III.1 *The fast collision operator $\mathcal{J}_i^{\mathcal{F}}(f)$, $i \in \mathrm{I}$, can be expanded in the form*

$$\mathcal{J}_i^{\mathcal{F}}(f) = \sum_{(j,i',j')\in\mathcal{F}_i} \mathcal{J}_{ij}^{i'j'(0)}(f_i, f_j) + \varepsilon \sum_{(j,i',j')\in\mathcal{F}_i} \mathcal{J}_{ij}^{i'j'(1)}(f_i, f_j) + \varepsilon^2 \sum_{(j,i',j')\in\mathcal{F}_i} \mathcal{J}_{ij}^{i'j'(2)}(f_i, f_j) + \mathcal{O}(\varepsilon^3). \tag{15}$$

Only the quasi-resonant collisions contribute to the terms that are higher than the zero-order term in the expansion.

The velocities after collision in eqs. (13) can be expanded in the ε parameter

$$\boldsymbol{c}_{i'} = \tilde{\boldsymbol{c}}_{i'} - \varepsilon \frac{E_{ij}^{i'j'(1)}}{|\boldsymbol{c}_i - \boldsymbol{c}_j|}\boldsymbol{\omega} - \varepsilon^2 \frac{(E_{ij}^{i'j'(1)})^2}{|\boldsymbol{c}_i - \boldsymbol{c}_j|^3}\boldsymbol{\omega} + \mathcal{O}(\varepsilon^3), \tag{16}$$

$$\boldsymbol{c}_{j'} = \tilde{\boldsymbol{c}}_{j'} + \varepsilon \frac{E_{ij}^{i'j'(1)}}{|\boldsymbol{c}_i - \boldsymbol{c}_j|}\boldsymbol{\omega} + \varepsilon^2 \frac{(E_{ij}^{i'j'(1)})^2}{|\boldsymbol{c}_i - \boldsymbol{c}_j|^3}\boldsymbol{\omega} + \mathcal{O}(\varepsilon^3), \tag{17}$$

where the modified velocities are introduced as there were no net internal energy through the collision

$$\tilde{\boldsymbol{c}}_{i'} = \tfrac{1}{2}(\boldsymbol{c}_i + \boldsymbol{c}_j) + \tfrac{1}{2}|\boldsymbol{c}_i - \boldsymbol{c}_j|\boldsymbol{\omega}, \tag{18}$$

$$\tilde{\boldsymbol{c}}_{j'} = \tfrac{1}{2}(\boldsymbol{c}_i + \boldsymbol{c}_j) - \tfrac{1}{2}|\boldsymbol{c}_i - \boldsymbol{c}_j|\boldsymbol{\omega}. \tag{19}$$

B. Enskog expansion

We employ an Enskog expansion to derive an approximate solution to the Boltzmann equations (8) by expanding the velocity distribution functions as

$$f_i = \hat{f}_i^0(1 + \varepsilon\hat{\phi}_i + \varepsilon^2\hat{\phi}_i^{(2)}) + \mathcal{O}(\varepsilon^3), \quad i \in \mathrm{I}. \tag{20}$$

and by imposing that the zero-order contribution $\hat{f}_i^0$ yields the local macroscopic properties

$$\langle\langle \hat{f}^0, \hat{\psi}^l \rangle\rangle = \langle\langle f, \hat{\psi}^l \rangle\rangle, \quad l \in \{1, \ldots, 6\}. \tag{21}$$

Using eq. (20), the nondimensional Boltzmann eq. (8) becomes

$$\mathcal{D}_i(\hat{f}_i^0) + \varepsilon\mathcal{D}_i(\hat{f}_i^0\hat{\phi}_i) + \mathcal{O}(\varepsilon^2) = \varepsilon^{-1}\mathcal{J}_i^{(-1)}(\hat{f}^0) + \mathcal{J}_i^{(0)}(\hat{f}^0, \hat{\phi}) + \varepsilon\mathcal{J}_i^{(1)}(\hat{f}^0, \hat{\phi}, \hat{\phi}^{(2)}) + \mathcal{O}(\varepsilon^2), \quad i \in \mathrm{I}, \tag{22}$$

where the collision operators at successive orders of the ε perturbation parameter are introduced in Appendix A.

In the Chapman-Enskog method, the gas is described at successive orders of the ε parameter as equivalent to as many time scales. The micro- and macroscopic equations derived at each order are reviewed in Table 2.

Order	Time	Microscopic	Macroscopic
ε^{-1}	τ^0	Equation for $\hat{f}_i^0$, $i \in \mathrm{I}$	Thermalization
ε^0	t^0	Equation for $\hat{\phi}_i$, $i \in \mathrm{I}$	Euler equations
ε^1	t^0/ε	Equation for $\hat{\phi}_i^{(2)}$, $i \in \mathrm{I}$	Navier-Stokes equations

Table 2. Chapman-Enskog steps.

C. Macroscopic conservation equations

We solve the heavy-particle Boltzmann eq. (22) at order ε^{-1} corresponding to the kinetic time scale τ^0. Let us introduce a temperature based on the perturbed internal energy though the implicit relation $\hat{\mathcal{E}}(\hat{T}_{int}) = \sum_{j\in\mathrm{I}} a_j\hat{E}_j \exp(-\hat{E}_j/\hat{T}_{int})/\hat{Q}$, where the perturbed internal partition function is given by the relation $\hat{Q}(\hat{T}_{int}) = \sum_{j\in\mathrm{I}} a_j \exp(-\hat{E}_j/\hat{T}_{int})$. The gas particle population is shown to thermalize to a quasi-equilibrium state described by a Maxwell-Boltzmann distribution function in thermal nonequilibrium with the translational energy at temperature T and the internal energy at temperature $\hat{T}_{int}$.

Proposition III.1 *The zero-order family of distribution functions $\hat{f}^0$ solution to eq. (22) at order ε^{-1}, i.e., $\mathcal{J}_i^{(-1)}(\hat{f}^0) = 0$, $i \in \mathrm{I}$, that satisfies the scalar constraints (21), is a family of Maxwell-Boltzmann distribution functions*

$$\hat{f}_i^0 = n\left(\frac{m}{2\pi T}\right)^{3/2}\frac{a_i}{\hat{Q}}\exp\left(-\frac{m}{2T}|\boldsymbol{c}_i - \boldsymbol{v}|^2 - \frac{\hat{E}_i}{\hat{T}_{int}}\right), \quad i \in \mathrm{I}. \tag{23}$$

The number density is defined as $n = \rho/m$. Only the fast collisions contribute to the collision operator $\mathcal{J}_i^{(-1)}(\hat{f}^0)$, $i \in \mathrm{I}$, the role of the fast collisions is the thermalization of the translational and internal energy modes.

We derive Euler equations based on the heavy-particle Boltzmann equation (22) at order ε^0 corresponding to the macroscopic time scale t^0. First, a linearized collision operator is introduced for fast collisions.

$$\mathcal{F}_i(\hat{\phi}) = -\frac{1}{\hat{f}_i^0}\sum_{(j,i',j')\in\mathcal{F}_i}\left[\mathcal{J}_{ij}^{i'j'(0)}(\hat{f}_i^0\hat{\phi}_i, \hat{f}_j^0) + \mathcal{J}_{ij}^{i'j'(0)}(\hat{f}_i^0, \hat{f}_j^0\hat{\phi}_j)\right] \quad i \in \mathrm{I},$$

where $\hat{f}_i^0$, $i \in \mathrm{I}$, is given by eq. (23), for a family $\hat{\phi} = (\hat{\phi}_i)_{i\in\mathrm{I}}$. The kernel of $\mathcal{F}$ is given in the following property.

Property III.2 *The kernel of the linearized collision operator $\mathcal{F}$ is the space of fast collisional invariants, i.e.,*

$$\langle\!\langle \hat{\psi}^l, \mathcal{F} \rangle\!\rangle = 0, \text{ for all } l \in \{1, \ldots, 6\}.$$

Furthermore, we define the pressure, as $p = nT$, and the energy transfered from the translational energy mode to the internal energy mode at order zero, as

$$\begin{aligned} \Delta E^0 &= \langle\!\langle \big[\sum_{(j,i',j') \in \mathcal{S}_i} \mathcal{J}_{ij}^{i'j'}(\hat{f}_i^0, \hat{f}_j^0) \big]_{i \in \mathrm{I}}, \hat{\psi}^5 \rangle\!\rangle \\ &= \sum_{(j,i',j') \in \mathcal{S}_i} \frac{T}{\tau_{ij}^{i'j'}} \left[\exp\left(\frac{E_{ij}^{i'j'}}{T} - \frac{\hat{E}_{ij}^{i'j'}}{\hat{T}_{int}} \right) - 1 \right]. \end{aligned} \tag{24}$$

Then, the Euler equations are derived in the following proposition.

Proposition III.2 *If $\hat{\phi}$ is a solution to eq. (22) at order ε^0, i.e.*

$$\hat{f}_i^0 \mathcal{F}_i(\hat{\phi}) = -\mathcal{D}_i(\hat{f}_i^0) + \check{\mathcal{J}}_i^{(0)}(\hat{f}^0), \quad i \in \mathrm{I}, \tag{25}$$

where $\hat{f}_i^0$, $i \in \mathrm{I}$, is given by eq. (23), and if $\hat{f}^0 \hat{\phi} = (\hat{f}_i^0 \hat{\phi}_i)_{i \in \mathrm{I}}$ satisfies the constraints

$$\langle\!\langle \hat{f}^0 \hat{\phi}, \hat{\psi}^l \rangle\!\rangle = 0, \quad l \in \{1, \ldots, 6\}, \tag{26}$$

then, the zero-order conservation equations of mass, momentum, translational energy, and perturbed internal energy read

$$\partial_t \rho + \boldsymbol{\partial_x} \cdot (\rho \boldsymbol{v}) = 0, \tag{27}$$

$$\partial_t (\rho \boldsymbol{v}) + \boldsymbol{\partial_x} \cdot (\rho \boldsymbol{v} \otimes \boldsymbol{v} + \tfrac{1}{M^2} p \mathbb{I}) = 0, \tag{28}$$

$$\partial_t (\tfrac{1}{2} \rho |\boldsymbol{v}|^2 + \rho e) + \boldsymbol{\partial_x} \cdot \big((\tfrac{1}{2} \rho |\boldsymbol{v}|^2 + \rho e + p) \boldsymbol{v} \big) = \Delta E^0, \tag{29}$$

$$\partial_t (\rho \hat{\mathcal{E}}) + \boldsymbol{\partial_x} \cdot (\rho \hat{\mathcal{E}} \boldsymbol{v}) = -\Delta E^0. \tag{30}$$

By inspecting eqs. (24) and (29)-(30), the role of the slow collisions becomes clear: they contribute to the thermal relaxation of the translational and internal energy modes.

IV. Conclusion and future work

In this paper, we have proposed a model for the internal energy excitation of a molecular gas in thermal nonequilibrium based on kinetic theory. The scaling of the Boltzmann equation is based on a dimensional analysis. The collisions are divided in two categories based on the magnitude of the net internal energy. For fast collisions, this quantity is assumed to be lower than an energy threshold equal to a fraction of a characteristic thermal energy for the gas controlled by a small parameter. The slow collisions are assumed to have a reference differential cross-section equal to a fraction of the one of the fast collisions. The Knudsen number is assumed to be proportional to this perturbation parameter, allowing for a continuum description of the system.

A lemma allows to split the internal energy of all the levels into perturbed elastic and inelastic contributions for the fast collisions. The introduction of perturbed energy levels is crucial to separate the energy collision invariant into fast collisional invariants. As opposed to conventional perturbations methods,[1,16] the fast collision operator is expanded in the small parameter used to define the threshold for the net energy for fast collisions. The gas particle population is shown to thermalize to a quasi-equilibrium state described by a Maxwell-Boltzmann distribution function in thermal nonequilibrium with the translational energy temperature and the internal energy temperature. The role of the fast collisions is the thermalization of the translational and internal energy modes. Euler equations for the conservation of the mass, momentum, translational energy, and internal energy are also derived. The role of the slow collisions is to contribute to the thermal relaxation of the translational and internal energy modes.

As future work, we propose to use the Chapman-Enskog method to derive the Navier-Stokes equations at the first order and account consistently for the inelastic contribution of the perturbed energy at the macroscopic level.

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A. Collision operators

The collision operators at successive orders of the ε perturbation parameter are introduced as

$$
\begin{aligned}
\mathcal{J}_i^{(-1)}(\hat{f}^0) &= \sum_{(j,i',j')\in\mathcal{F}_i} \mathcal{J}_{ij}^{i'j'(0)}(\hat{f}_i^0,\hat{f}_j^0),\\
\mathcal{J}_i^{(0)}(\hat{f}^0,\hat{\phi}) &= \sum_{(j,i',j')\in\mathcal{F}_i} \left[\mathcal{J}_{ij}^{i'j'(0)}(\hat{f}_i^0\hat{\phi}_i,\hat{f}_j^0)+\mathcal{J}_{ij}^{i'j'(0)}(\hat{f}_i^0,\hat{f}_j^0\hat{\phi}_j)\right]+\check{\mathcal{J}}_i^{(0)}(\hat{f}^0),\\
\check{\mathcal{J}}_i^{(0)}(\hat{f}^0) &= \sum_{(j,i',j')\in\mathcal{F}_i} \mathcal{J}_{ij}^{i'j'(1)}(\hat{f}_i^0,\hat{f}_j^0)+\sum_{(j,i',j')\in\mathcal{S}_i} \mathcal{J}_{ij}^{i'j'}(\hat{f}_i^0,\hat{f}_j^0),\\
\mathcal{J}_i^{(1)}(\hat{f}^0,\hat{\phi},\hat{\phi}^{(2)}) &= \sum_{(j,i',j')\in\mathcal{F}_i} \left[\mathcal{J}_{ij}^{i'j'(0)}(\hat{f}_i^0\hat{\phi}_i^{(2)},\hat{f}_j^0)+\mathcal{J}_{ij}^{i'j'(0)}(\hat{f}_i^0,\hat{f}_j^0\hat{\phi}_j^{(2)})\right]+\check{\mathcal{J}}_i^{(1)}(\hat{f}^0,\hat{\phi}),\\
\check{\mathcal{J}}_i^{(1)}(\hat{f}^0,\hat{\phi}) &= \sum_{(j,i',j')\in\mathcal{F}_i} \left[\mathcal{J}_{ij}^{i'j'(0)}(\hat{f}_i^0\hat{\phi}_i,\hat{f}_j^0\hat{\phi}_j)+\mathcal{J}_{ij}^{i'j'(1)}(\hat{f}_i^0\hat{\phi}_i,\hat{f}_j^0)+\mathcal{J}_{ij}^{i'j'(1)}(\hat{f}_i^0,\hat{f}_j^0\hat{\phi}_j)+\mathcal{J}_{ij}^{i'j'(2)}(\hat{f}_i^0,\hat{f}_j^0)\right]\\
&\quad+\sum_{(j,i',j')\in\mathcal{S}_i} \left[\mathcal{J}_{ij}^{i'j'}(\hat{f}_i^0\hat{\phi}_i,\hat{f}_j^0)+\mathcal{J}_{ij}^{i'j'}(\hat{f}_i^0,\hat{f}_j^0\hat{\phi}_j)\right].
\end{aligned}
$$

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